

Isotope effects and the charge gap formation in the charge ordered phase of colossal magnetoresistance manganites

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Giant oxygen isotope effects observed in colossal magnetoresistance manganites are investigated by employing the combined model of the double exchange and interacting lattice polaron mechanism. We have shown that the isotope effects on T_C in the metallic phase and T_{CO} in the charge ordered phase of manganites can be explained well in terms of the double exchange and polaron narrowing factors with reasonable physical parameters.

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A recent discovery of colossal magnetoresistance (CMR) phenomena has stimulated enormous interest in the perovskite manganites, $R_{1-x}A_x\text{MnO}_3$ (RAMO: R = rare-earth; A = divalent cation) [1,2]. They exhibit a very rich phase diagram depending on the doping concentration, temperature, and pressure: antiferromagnetic (AFM) insulator, ferromagnetic (FM) metal, charge ordered (CO) insulator [3]. These novel features suggest that several interactions originating from the spin, charge, and lattice degrees of freedom are competing. For instance, the correlation between ferromagnetism and metallic conductivity for $0.2 < x < 0.5$ was explained qualitatively in terms of the double exchange (DE) mechanism [4]. On the other hand, Jahn-Teller polaron effects due to a strong electron-phonon interaction are thought to be responsible for anomalous properties of manganites [5].

The most evident signature for the lattice degree of freedom is considered to be the isotope effect, because it can affect the electronic properties only through the electron-phonon interaction. Indeed many recent experiments, such as magnetization, resistivity, thermal expansion, electron paramagnetic resonance, and magnetostriction measurements, have revealed giant isotope effects both in the metallic and CO phases of RAMO [6–15]. The isotope effect on the magnetic phase transition temperature T_C in the metallic phase [6–9] and on the charge ordering transition temperature T_{CO} [10–15] were confirmed by replacing ^{16}O with ^{18}O . Zhao *et al.* [6] have obtained a shift of 20K in T_C in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, yielding the isotope exponent $\alpha_c = 0.85$ ($\alpha_c \equiv -\Delta \ln T_C / \Delta \ln M_O$, M_O : oxygen isotope mass). On the other hand, Franck *et al.* [9] obtained $\alpha_c \sim 0.4$ for the same Ca concentration. This large difference in α_c between two groups is suspected to arise from the different sample stoichiometry due to oxygen excess [9].

For the CO phases, Isaac *et al.* [11] observed ΔT_{CO} with a negative oxygen isotope exponent $\alpha_{co} = -0.41$ in $\text{La}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$. Further, novel crossovers from a metallic to a CO insulating ground state are observed in $(\text{La}_{0.5}\text{Nd}_{0.5})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ [10,12] and in $(\text{La}_{0.175}\text{Pr}_{0.525})\text{Ca}_{0.3}\text{MnO}_3$ [15] by the oxygen isotope exchange. The above systems are metallic with ^{16}O , but are very close to the phase boundary between the FM metal and the CO insulator. A more interesting feature is manifested in the CO phases of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [13,14], which show the strong magnetic field dependence of the isotope effect. Under the magnetic field of 5.4 T, ΔT_{CO} increases substantially from 21K to 43K for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, and from 9K to 40K for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, respectively. Thus, the magnitude of $\alpha_{co} (\equiv -\Delta \ln T_{CO} / \Delta \ln M_O)$ increases rapidly with the magnetic field. This feature is in contrast to the case of α_c in the metallic phase that is rather insensitive to the magnetic field [9,14]. It has been pointed out that these anomalous features are difficult to understand within the existing theories of the charge ordering transition [13,14].

The isotope effects in the metallic phase can be explained properly by using the small polaron model [6]. In contrast, the understanding of the isotope effects in the CO phase is not straightforward. In the previous study [16], we have described successfully the lattice and magnetic properties of the CO phase of half-doped Mn-oxides using the combined model of the double exchange and interacting lattice polaron mechanism. The electron lattice of the CO state was viewed as the generalized Wigner crystal, that is, the CO state becomes stable when the repulsive Coulomb interaction between carriers dominates over the kinetic energy of carriers. In this paper, we have explored the isotope effects in the CO phase of CMR manganites on the basis of the similar model. We have found that the isotope effects and related features in the CO phase of manganites are well described in terms of the present model.

Let us first examine the isotope effect in the metallic phase. The standard small polaron theory shows that the strong electron-phonon interaction reduces the electron hopping parameter by the polaron narrowing factor [17],

$$\tilde{t} = t \exp \left[- \sum_{\mathbf{q}} |u_{\mathbf{q}}|^2 (N_{\mathbf{q}} + 1/2) \right] \quad (1)$$

with $u_{\mathbf{q}} = M_q / \omega_q (\exp(i\mathbf{q} \cdot \boldsymbol{\delta}) - 1)$. Here M_q is the parameter of the electron-phonon interaction strength, ω_q is the

phonon frequency, N_q is the boson distribution function, and δ is the displacement to the neighboring site. The electron-phonon interaction parameter M_q depends both on the ion mass and the phonon frequency in the form of $M_q \sim (M_{ion}\omega)^{-1/2}$. Hence $\sum |u_q|^2$ is proportional to $\sqrt{M_{ion}}$ with the assumption of $\omega \sim (M_{ion})^{-1/2}$. In the DE model, T_C is proportional to the hopping parameter [18], *i.e.*, $T_C \sim \tilde{t} \sim t \exp[-\gamma\sqrt{M_{ion}}]$, and so the material with heavier ion mass would have the lower T_C . This is nothing but the isotope effect observed in the metallic phase of RAMO. Note that, with increasing $\sum_q |u_q|^2$, one gets the larger isotope effect.

The experimental results of Franck *et al.* ($\alpha_c = 0.34$) [9] can be reproduced with $\sum_q |u_q|^2 = 1.2$ and $\omega = 0.07\text{eV}$. In the same framework, one can also explain the reduction of α_c with increasing the tolerance factor [6,9]. The increase of the tolerance factor leads to the increase of the Mn–O–Mn bond angle and the decrease of the bond length between neighboring Mn sites [19]. One can thus expect that the phonon frequency becomes hardened due to reduced bond length [20], and accordingly $\sum_q |u_q|^2$ decreases considering $\sum_q |u_q|^2 \sim (\omega)^{-3}$. Therefore, we have smaller α_c with increasing the tolerance factor in agreement with the observation. In addition, the increase of the Mn–O–Mn bond angle and the decrease of bond length will certainly increase the hopping parameter and so weakens the polaron formation [21]. This effect plays a role of reducing $\sum_q |u_q|^2$ and α_c further.

As for the giant isotope effects in manganites, Nagaev [22] has proposed mechanisms which are not related to the electron-phonon interaction. He claimed that a change in the oxygen isotope leads inevitably to a change in the sample stoichiometry. So thermodynamic equilibrium densities of oxygen vacancies or excess oxygen atoms depend on the mass of the oxygen atom and so corresponding carrier density has isotope dependence. In addition, the oxygen nonstoichiometry (vacancies) produces the isotope dependent pressure by causing a change in the volume. These mechanisms seem to explain observed isotope effects in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ which are very sample dependent ($\alpha_c=0.85$ vs. $\alpha_c \sim 0.4$), as mentioned above. This scenario, however, works only for the low carrier density regime ($x < 3/8$). Moreover, more recent experiments have shown that there are intrinsic isotope effects which are not caused by any possible differences in the oxygen content [9,10]. Also it is hard to explain with these mechanisms the isotope effects in the CO phase of manganites.

Now let us consider the isotope effect in the CO phase. Since T_{CO} is not linearly proportional to the hopping parameter in this case, one has to find the relation between T_{CO} and the hopping parameter. The extended polaron Hamiltonian for the half-doped manganites incorporating the electron-phonon interaction is expressed as

$$H = \sum_{ij} t_{ij}^D c_i^\dagger c_j + \frac{1}{2} V_0 \sum_{\langle ij \rangle} n_i n_j + \sum_{\mathbf{q}} \omega_q a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{j\mathbf{q}} c_j^\dagger c_j e^{i\mathbf{q} \cdot \mathbf{R}_j} M_q (a_{\mathbf{q}} + a_{-\mathbf{q}}^\dagger), \quad (2)$$

where $t_{ij}^D (\equiv t \langle \cos \frac{\theta}{2} \rangle)$, θ : angle between two spins on neighboring sites) is the DE hopping parameter and V_0 is the Coulomb repulsion between two electrons of neighboring sites. Using the polaron canonical transformation, one can get

$$\bar{H} = \sum_{ij} \tilde{t}_{ij}^D c_i^\dagger c_j + \frac{1}{2} V \sum_{\langle ij \rangle} n_i n_j + \sum_{\mathbf{q}} \omega_q a_{\mathbf{q}}^\dagger a_{\mathbf{q}} - \sum_j n_j \Delta_p, \quad (3)$$

where $V (\equiv V_0 - 2 \sum_{\mathbf{q}} \frac{M_q^2}{\omega_q} \exp(i\mathbf{q} \cdot \delta))$ corresponds to the renormalized Coulomb repulsion and $\Delta_p (\equiv \sum_{\mathbf{q}} \frac{M_q^2}{\omega_q})$ is the polaron binding energy. The effective hopping \tilde{t}^D is defined as in Eq. (1) with the bare hopping t replaced by t^D . It can be shown that V does not depend on the ion mass when $\omega \sim (M_{ion})^{-1/2}$. Thus the isotope effects will be realized only through \tilde{t}^D , if they exist.

To describe the CO state in the mean field approximation, the size of the unit cell is doubled by introducing formally two identical sublattices. This procedure automatically implies that the CO state can be only of a checkerboard type and certain restrictions are put on the lattice symmetry. Also, for simplicity, the electron hopping will be permitted only between sites belonging to different sublattices. Then the electronic part of the above Hamiltonian is reduced to the following form:

$$\bar{H} = \sum_{\alpha \neq \beta} \tilde{t}_{\alpha\beta}^D a_\alpha^\dagger a_\beta + zV\tau \sum_{\alpha} (-1)^\alpha a_\alpha^\dagger a_\alpha, \quad (4)$$

where α and β are sublattice indices, z is the number of nearest neighbors, and τ is the charge ordering order parameter ($-0.5 \leq \tau \leq 0.5$), describing the deviation in electron concentration in the CO phase, *i.e.*, $n_\alpha = \frac{1}{2} + \tau$; $n_\beta = \frac{1}{2} - \tau$.

Diagonalizing the above Hamiltonian, one gets two states with energy $\pm \epsilon(k)$, where $\epsilon(k) = \sqrt{|\tilde{t}^D(k)|^2 + (zV\tau)^2}$ [23]. Therefore, in the CO phase, the initial band is split into two bands with a charge gap of $2\Delta = 2zV\tau$. The order parameter τ can be determined from the following BCS-like self-consistent equation,

$$1 = \frac{zV}{2} \frac{1}{N} \sum_k \frac{\tanh(\beta\epsilon(k)/2)}{\epsilon(k)}, \quad (5)$$

where $\beta = \frac{1}{k_B T}$. The wave vector summation in Eq. (5) can be replaced by the energy integration with the appropriate density of states (DOS). In the case of three-dimensional (3D) system, the DOS without the charge ordering $\rho_0(\epsilon)$ can be chosen as a semielliptic form, $\rho_0(\epsilon) = \frac{4}{\pi B^2} \sqrt{B^2 - \epsilon^2}$, where $B(\equiv z\tilde{t}^D)$ is a half of the bandwidth without the charge ordering. Then the self-consistent equation at $T = 0$ reads $1 = \frac{2}{\pi} \frac{\sqrt{b^2 + \tau^2}}{b^2} \left(K \left(\sqrt{\frac{b^2}{b^2 + \tau^2}} \right) - E \left(\sqrt{\frac{b^2}{b^2 + \tau^2}} \right) \right)$, where $b = \frac{B}{zV}$, and $K(k)$ and $E(k)$ are elliptic integral of the first and the second kind, respectively.

By expanding the elliptic integrals into series in both the narrow and wide band width limits, the analytic form of the charge gap can be obtained: $\Delta_0 \approx \frac{zV}{2} \left(1 - \frac{1}{2} \left(\frac{B}{zV} \right)^2 \right)$ for $\frac{B}{zV} \ll 1$, and $\Delta_0 = 4B e^{-\left(\frac{\pi B}{2zV} + 1\right)}$ for $\frac{B}{zV} \gg 1$. Figure 1 provides the overall behavior of Δ_0 as a function of the band width. It is seen that Δ_0 diminishes with increasing the hopping parameter, suggesting that the transition between the CO and the charge disordered state can be described by the competition between the hopping and the intersite Coulomb repulsion parameter.

The self-consistent equation Eq. (5) also determines the charge ordering temperature T_{CO} . At T_{CO} , the charge gap is closed in the spectrum and the order parameter τ is equal to zero. In the narrow band limit, $\frac{B}{zV} \ll 1$, the \tanh function in Eq. (5) can be expanded into the series. Then T_{CO} is given by $k_B T_{CO} \approx \frac{zV}{4} \left(1 - \frac{1}{3} \left(\frac{B}{zV} \right)^2 \right)$. Hence for the dispersionless band, it follows that $k_B T_{CO} \approx \frac{zV}{4} = \frac{\Delta_0}{2}$, in accordance with the previous work [16]. In the opposite case of the wide band limit, $\frac{B}{zV} \gg 1$, T_{CO} can be obtained through the procedure analogous to the BCS theory [24]. Careful retaining of all the terms that do not vanish under $\frac{B}{k_B T_{CO}} \rightarrow \infty$ shows that the BCS result is obtained despite the nonconstant DOS of the present band, $k_B T_{CO} = \frac{e^\gamma}{\pi} \Delta_0 \approx 0.567 \Delta_0$, where γ is the Euler constant (~ 0.5772). Thus, the ratio of $\frac{\Delta_0}{k_B T_{CO}}$ does not change significantly with varying the ratio of $\frac{B}{zV}$.

Overall dependence of T_{CO} on $\frac{B}{zV}$ is presented in Fig. 2. Note that T_{CO} is $zV/4$ at $B = 0$ and diminishes as B becomes larger. The observed decrease of T_{CO} and the concomitant collapse of the CO state in half-doped manganites by applying the magnetic field or the pressure can be qualitatively understood in this context [25]. That is, the magnetic field or the pressure increases the bandwidth to induce the instability of the CO state.

Now, based on the above relation of T_{CO} with the effective hopping parameter \tilde{t}^D , one can account for the isotope effects observed in the CO phase. Since \tilde{t}^D has ion mass dependence in the expression of the polaron narrowing factor, the replacement of ^{16}O with heavier ^{18}O gives rise to a smaller \tilde{t}^D and so yields enhanced T_{CO} . Let us estimate the reasonable physical parameters producing the experimental isotope exponent α_{co} . For a given $T_{CO} = 150\text{K}$, one can have $t^D = 0.05\text{eV}$, $\sum_{\mathbf{q}} |u_{\mathbf{q}}|^2 = 1.2$, and the screened Coulomb repulsion $V = 0.018\text{eV}$. The bare hopping parameter t^D in the CO phase is thought to be smaller than that in the metallic phase because of the different spin ordering fluctuations. With these parameters, one could get the isotope exponent $\alpha_{co} = -0.44$ that is consistent with experiments [11,14].

The isotope induced crossover from a metallic to a CO insulating ground state [10,12,15] can be explained in the same way. The heavier ion mass of ^{18}O reduces \tilde{t} , and so both T_C and the insulator to metal transition temperature T_{MI} decrease. In contrast, T_{CO} increases with decreasing \tilde{t} , so that the CO insulating ground state becomes stabilized by the isotope exchange. One can also understand the anomalous isotope effects observed in the CO phases of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ under the strong magnetic field [13,14]. In the presence of the magnetic field, \tilde{t}^D increases due to the DE term $\langle \cos \frac{\theta}{2} \rangle$ and this will in turn reduce T_{CO} . Under this circumstance, the isotope substitution of ^{18}O reduces \tilde{t}^D much more rapidly than the case without the magnetic field because of larger DE term, and so enhances the isotope exponent α_{co} . This effect is clearly demonstrated in Fig. 3 which plots $-\alpha_{co}$ as a function of the bare DE hopping parameter t^D . The magnitude of α_{co} becomes larger with increasing t^D , which corresponds to the case of applying the magnetic field. Direct comparison with the experiments may be possible, once the precise functional relation between t^D and the magnetic field is known. The variation of $-\alpha_{co}$ with t^D and the corresponding physical parameters seem qualitatively consistent with observations [13,14], indicating that the present argument describes the main physics of isotope effects in the CO phase of RAMO.

It is noteworthy that similar arguments were provided recently by Babushkina *et al.* [26] in analyzing their isotope induced metal-insulator transition in $(\text{La}_{0.175}\text{Pr}_{0.525})\text{Ca}_{0.3}\text{MnO}_3$. In their model, the isotope effect is caused by the modification of the effective hopping integrals due to the change of interatomic distance by lattice vibrations. They obtained the relation between T_{CO} and the effective hopping parameter, and speculated that the large isotope effect arises from the hopping parameter that is very close to a certain critical value, $t_c = zV/2$. In fact, this result corresponds to the present one in the narrow band limit $\frac{B}{zV} \ll 1$. So their model is valid only in this limit. Further, they did not consider the polaron effect, so that the isotope mass dependence of the effective hopping integral is weak, $\sim \frac{1}{\sqrt{M}}$, as opposed to the present case $\sim \exp \left[-\sqrt{M} \right]$. Accordingly, their model is difficult to apply to the analysis of

the anomalous isotope effects in the presence of the magnetic field [13,14].

To summarize, we have studied the isotope effects both in the metallic phase and the CO phase of RAMO, using the combined model of the double exchange and the interacting lattice polaron mechanism. We have investigated the charge ordering transition in the mean-field approximation, and obtained the relation between T_{CO} and the effective hopping parameter. From this, we have shown that the various isotope effects including the magnetic field induced enhancement of α_{co} in the CO phase of half-doped manganites can be explained in a natural way.

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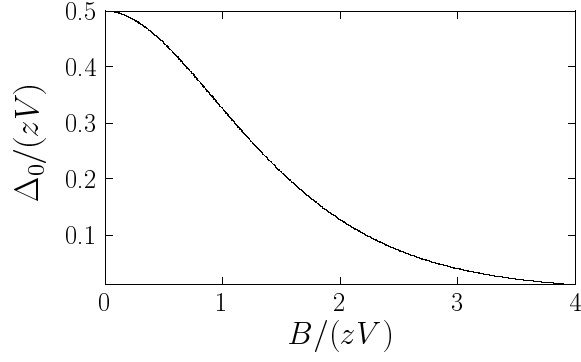


FIG. 1. The zero temperature charge gap Δ_0 as a function of the half-bandwidth $B (= z\tilde{t}^D)$ for the model 3D system. The values are scaled by zV where z is the number of nearest neighbors and V is the renormalized Coulomb interaction between carriers.

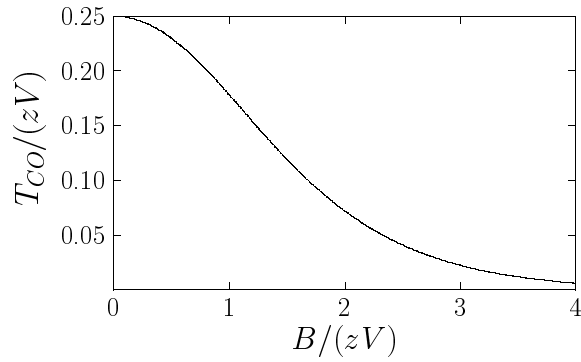


FIG. 2. The charge ordering transition temperature T_{CO} as a function of half-bandwidth B .

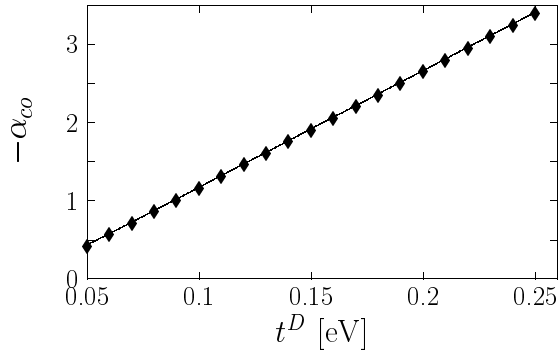


FIG. 3. The absolute value of the oxygen isotope exponent ($-\alpha_{co}$) as a function of the bare DE hopping parameter t^D . Calculations are performed for the parameters, $\sum_{\mathbf{q}} |u_{\mathbf{q}}|^2 = 1.2$, $V = 0.018\text{eV}$, $T_{CO} = 150\text{K}$, $\omega = 0.07\text{eV}$.